

WE CLAIM:

1. A thermal barrier coating for coating a substrate, comprising:  
a bond coating layer disposed on a surface of said substrate;  
a segmented columnar ceramic layer disposed on said bond coating layer, said segmented columnar ceramic layer comprising a layer of  
5 stabilized hafnia, said layer of stabilized hafnia having a plurality of segmentation gaps therein; and  
a structure-stabilizing material disposed within said plurality of segmentation gaps, wherein said structure-stabilizing material is interposed between adjacent columns within said segmented columnar ceramic layer.
2. The thermal barrier coating of claim 1, wherein said segmented columnar ceramic layer comprises a layer of yttria stabilized hafnia.
3. The thermal barrier coating of claim 1, wherein said structure-stabilizing material is a reaction product formed by reacting a first sol gel component with a second sol gel component.
4. The thermal barrier coating of claim 1, wherein said layer of stabilized hafnia includes a stabilizing oxide component, and said structure-stabilizing material is a reaction product formed by reacting a sol gel component with said stabilizing oxide component.
5. The thermal barrier coating of claim 1, wherein said structure-stabilizing material comprises particles of an yttrium aluminum oxide.
6. The thermal barrier coating of claim 1, wherein said structure-stabilizing material is insoluble in said layer of stabilized hafnia at a temperature of at least about 3400°F.

7. The thermal barrier coating of claim 1, wherein said structure-stabilizing material is selected from the group consisting of  $\text{YAlO}_3$ ,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and  $\text{Y}_4\text{Al}_2\text{O}_9$ .

8. The thermal barrier coating of claim 1, further comprising a sealant layer disposed on said layer of stabilized hafnia, said sealant layer sealing said plurality of segmentation gaps.

9. The thermal barrier coating of claim 8, wherein said layer of stabilized hafnia comprises yttria stabilized hafnia.

10. The thermal barrier coating of claim 8, wherein said sealant layer comprises a continuous, non-segmented layer of cubic yttria stabilized hafnia or a continuous, non-segmented layer of cubic yttria stabilized zirconia.

11. The thermal barrier coating of claim 8, wherein said sealant layer has a thickness in the range of from about 0.5 to 10 mils.

12. The thermal barrier coating of claim 1, wherein said layer of stabilized hafnia comprises cubic yttria stabilized hafnia and has a thickness in the range of from about 10 to 60 mils.

13. The thermal barrier coating of claim 1, wherein said segmented columnar ceramic layer further comprises a layer of stabilized zirconia, said layer of stabilized zirconia disposed on said bond coating layer, and said layer of stabilized hafnia disposed on said layer of stabilized zirconia.

14. The thermal barrier coating of claim 13, wherein said layer of stabilized zirconia comprises a layer of yttria stabilized zirconia, and said layer

of stabilized hafnia comprises a layer of yttria stabilized hafnia.

15. The thermal barrier coating of claim 13, wherein a discrete interface exists between said layer of stabilized zirconia and said layer of stabilized hafnia.

16. The thermal barrier coating of claim 13, wherein said layer of stabilized zirconia transitions to said layer of stabilized hafnia through a concentration gradient comprising varying concentrations of stabilized zirconia and stabilized hafnia.

17. A thermal barrier coating for coating a substrate, comprising:  
a bond coating layer disposed on a surface of said substrate;  
a first segmented columnar ceramic layer comprising yttria  
stabilized zirconia disposed on said bond coating layer;  
5 a second segmented columnar ceramic layer comprising yttria  
stabilized hafnia disposed on said first segmented columnar ceramic layer,  
each of said first segmented columnar ceramic layer and said second  
segmented columnar ceramic layer having a plurality of segmentation gaps  
therein;  
10 a structure-stabilizing material disposed within said plurality of  
segmentation gaps, wherein said structure-stabilizing material stabilizes said  
first segmented columnar ceramic layer and said second segmented columnar  
ceramic layer; and  
an outer sealant layer disposed on said second segmented  
15 columnar ceramic layer, said outer sealant layer comprising a continuous, non-  
segmented ceramic layer, and said outer sealant layer sealing said plurality of  
segmentation gaps within said second segmented columnar ceramic layer.

18. The thermal barrier coating of claim 17, wherein said plurality of

segmentation gaps within said first segmented columnar ceramic layer are substantially aligned with said plurality of segmentation gaps within said second segmented columnar ceramic layer.

19. The thermal barrier coating of claim 18, wherein said structure-stabilizing material is insoluble in said second segmented columnar ceramic layer when said second segmented columnar ceramic layer is exposed to a temperature of about 3400°F.

20. The thermal barrier coating of claim 17, wherein said first segmented columnar ceramic layer comprises cubic yttria stabilized zirconia, and said second segmented columnar ceramic layer comprises cubic yttria stabilized hafnia.

21. The thermal barrier coating of claim 20, wherein the thickness of said second segmented columnar ceramic layer is selected such that a temperature gradient transition within said thermal barrier coating from said cubic yttria stabilized zirconia to said cubic yttria stabilized hafnia occurs at a  
5 temperature of less than about 2900°F.

22. A thermal barrier coating for coating a substrate, comprising:  
a bond coating layer disposed on a surface of said substrate;  
a layer of cubic yttria stabilized zirconia disposed on said bond  
coating layer, said layer of cubic yttria stabilized zirconia comprising from about  
5 7 to 40 mole % yttria and from about 60 to 93 mole % zirconia, and having a  
thickness in the range of from about 5 to 60 mils;  
a layer of cubic yttria stabilized hafnia disposed on said layer of  
cubic yttria stabilized zirconia, said layer of cubic yttria stabilized hafnia having  
a thickness in the range of from about 5 to 50 mils, each of said layer of cubic  
10 yttria stabilized hafnia and said layer of cubic yttria stabilized zirconia having a

columnar microstructure and a plurality of segmentation gaps within said columnar microstructure, said plurality of segmentation gaps oriented substantially orthogonal to said surface of said substrate;

15 a structure-stabilizing material disposed within said plurality of segmentation gaps, said structure-stabilizing material comprising particles of an yttrium aluminum oxide, said particles having a diameter in the range of from about 0.1 to 2 microns; and

20 an outer sealant layer disposed on said layer of cubic yttria stabilized hafnia, said outer sealant layer comprising a continuous, non-segmented coating on said columnar microstructure, and said outer sealant layer sealing said plurality of segmentation gaps within said layer of cubic yttria stabilized hafnia, said outer sealant layer comprising a material selected from the group consisting of cubic yttria stabilized zirconia and cubic yttria stabilized hafnia.

23. In a thermal barrier coating including a bond coating layer, a first segmented columnar ceramic layer on the bond coating layer, and a structure-stabilizing material interposed between columns of said first segmented columnar ceramic layer, the improvement which comprises:

5 a second segmented columnar ceramic layer disposed on said first segmented columnar ceramic layer, said second segmented columnar ceramic layer comprising yttria stabilized hafnia, wherein said structure-stabilizing material is insoluble in said second segmented columnar ceramic layer at a temperature of at least about 3400°F.

24. The thermal barrier coating of claim 23, wherein said second segmented columnar ceramic layer and said first segmented columnar ceramic layer resist sintering when an outer surface of said thermal barrier coating is exposed to a temperature of at least about 3400°F.

25. The thermal barrier coating of claim 23, wherein said second segmented columnar ceramic layer comprises cubic yttria stabilized hafnia and said first segmented columnar ceramic layer comprises cubic yttria stabilized zirconia.

26. The thermal barrier coating of claim 23, further comprising a continuous, non-segmented ceramic sealant layer disposed on said second segmented columnar ceramic layer, wherein said sealant layer comprises a material selected from the group consisting of cubic stabilized zirconia and  
5 cubic stabilized hafnia.

27. The thermal barrier coating of claim 26, wherein said sealant layer comprises a material selected from the group consisting of cubic yttria stabilized zirconia and cubic yttria stabilized hafnia.

28. The thermal barrier coating of claim 23, wherein said sealant layer prevents penetration of glassy dust or salt deposits into said thermal barrier coating, and said thermal barrier coating promotes the elimination of glassy dust and salt deposits from said thermal barrier coating.

29. An article of manufacture for a gas turbine engine, comprising:  
a superalloy substrate;  
a bond coating layer disposed on said substrate;  
a first segmented columnar ceramic layer comprising yttria  
5 stabilized zirconia disposed on said bond coating layer;  
a second segmented columnar ceramic layer comprising yttria stabilized hafnia disposed on said first segmented columnar ceramic layer, each of said first segmented columnar ceramic layer and said second segmented columnar ceramic layer having a plurality of segmentation gaps  
10 therein, said plurality of segmentation gaps interspersed with and defining a

plurality of columns within said first and second segmented columnar ceramic layers;

15 a structure-stabilizing material disposed within said plurality of segmentation gaps, wherein said structure-stabilizing material maintains the integrity of said plurality of columns within said first segmented columnar ceramic layer and said second segmented columnar ceramic layer; and

an outer, continuous, non-segmented sealant layer disposed on said second segmented columnar ceramic layer, said sealant layer preventing penetration of extraneous materials into said plurality of segmentation gaps.

30. The article of manufacture of claim 29, wherein said structure-stabilizing material comprises particles of an yttrium aluminum oxide, said particles interposed between adjacent members of said plurality of columns, said particles having a diameter in the range of from about 0.1 to 2 microns.

31. The article of manufacture of claim 29, wherein said bond coating layer is selected from the group consisting of an aluminide and a MCrAlY, wherein M is a metal selected from the group consisting of nickel, cobalt, and mixtures thereof.

32. A method of forming a thermal barrier coating on a substrate, comprising:

- a) providing said substrate;
- b) depositing a bond coating layer on a surface of said substrate;
- 5 c) depositing a segmented columnar ceramic layer on said bond coating layer such that said segmented columnar ceramic layer has a plurality of segmentation gaps therein and a plurality of columns defining said plurality of segmentation gaps, said segmented columnar ceramic layer comprising a layer of yttria stabilized hafnia; and
- 10 d) depositing a structure-stabilizing material within said plurality of

segmentation gaps.

33. The method of claim 32, wherein said segmented columnar ceramic layer further comprises a layer of yttria stabilized zirconia, said layer of yttria stabilized zirconia deposited on said bond coating layer, and said layer of yttria stabilized hafnia disposed on said layer of yttria stabilized zirconia.

34. The method of claim 32, wherein said layer of yttria stabilized hafnia comprises cubic yttria stabilized hafnia, said structure-stabilizing material comprises at least one yttrium aluminum oxide, and said structure-stabilizing material is insoluble in said layer of yttria stabilized hafnia at a temperature of at least about 3400°F.

35. The method of claim 32, wherein said step d) comprises:  
e) infiltrating a sol gel solution into said plurality of segmentation gaps, wherein said sol gel solution comprises a first sol gel component comprising an alkoxide of yttrium.

36. The method of claim 35, wherein said sol gel solution further comprises a second sol gel component comprising an alkoxide of aluminum; and said step d) further comprises:

f) after said step e), reacting said first sol gel component with said second sol gel component to form at least one yttrium aluminum oxide.

37. The method of claim 36, further comprising, after said step f), exposing said infiltrated first and second sol gel components to a heat treatment, whereby particles of said structure-stabilizing material are formed within said plurality of segmentation gaps, and said particles of said structure-stabilizing material are strongly bound to said plurality of columns.



38. The method of claim 37, wherein said structure-stabilizing material comprises at least one oxide selected from the group consisting of  $\text{YAlO}_3$ ,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and  $\text{Y}_4\text{Al}_2\text{O}_9$ .

39. The method of claim 32, further comprising:

g) depositing a continuous, non-segmented sealant layer on said segmented columnar ceramic layer, wherein said sealant layer seals said segmentation gaps, whereby said sealant layer prevents extraneous materials  
5 from penetrating said thermal barrier coating.

40. The method of claim 32, further comprising:

h) forming a plurality of effusion holes through said bond coating layer and said segmented columnar ceramic layer, wherein said plurality of effusion holes are formed at an angle of from about  $10^\circ$  to  $30^\circ$  with respect to  
5 said surface of said substrate.

41. The method of claim 33, wherein said layer of yttria stabilized zirconia comprises cubic yttria stabilized zirconia, and said layer of yttria stabilized hafnia comprises cubic yttria stabilized hafnia.

42. A method of making an article of manufacture, comprising:

a) providing a substrate;  
b) depositing a bond coating layer on a surface of said substrate;  
c) depositing a first segmented columnar ceramic layer on said  
5 bond coating layer, said first segmented columnar ceramic layer comprising yttria stabilized zirconia;  
d) depositing a second segmented columnar ceramic layer on said first segmented columnar ceramic layer, said second segmented columnar ceramic layer comprising yttria stabilized hafnia, wherein said first segmented  
10 columnar ceramic layer and said second segmented columnar ceramic layer

have a plurality of segmentation gaps therein;

15 e) depositing particles of a structure-stabilizing material within said plurality of segmentation gaps, wherein said particles of structure-stabilizing material inhibit sintering of at least one of said first segmented columnar ceramic layer and said second segmented columnar ceramic layer; and

20 f) depositing a continuous, non-segmented sealant layer on said second segmented columnar ceramic layer, said sealant layer comprising cubic yttria stabilized hafnia or cubic yttria stabilized zirconia, and wherein said sealant layer prevents ingress of extraneous materials into said first and second segmented columnar ceramic layers.

43. The method of claim 42, wherein said step e) comprises:

g) infiltrating a sol gel solution comprising an yttrium alkoxide and an aluminum alkoxide into said plurality of segmentation gaps; and

5 h) heating said infiltrated sol gel solution at a temperature in the range of from about 400°C to 700°C to form particles of at least one yttrium aluminum oxide within said plurality of segmentation gaps.

44. The method of claim 42, wherein said substrate comprises a superalloy substrate, and said article of manufacture comprises a combustor, a liner, a shroud, or an airfoil for a gas turbine engine.

45. The method of claim 43, wherein said infiltrated sol gel solution has a viscosity in the range of from about 1 to 10 centipoise.

46. The method of claim 42, wherein said step e) comprises:

5 g) infiltrating a sol gel solution comprising an aluminum alkoxide into said plurality of segmentation gaps; and

h) heating said infiltrated sol gel solution at a temperature in the range of from about 400°C to 700°C to form particles of aluminum oxide within

- said plurality of segmentation gaps; and
- 10                    i) thermally reacting alumina particles with the yttria stabilizer of the columnar ceramic to form particles of at least one yttrium aluminum oxide, wherein the thermal reaction occurs during exposure of the thermal barrier coated component to high-temperature service.